On Attempts to Synthesize Lanthanide Complexes of the Dianionic Fluorenyl-alkoxo Ligand $[C_{13}H_8$-*cyclo*-C_6H_{10}-$O]^{2-}$. Crystal Structure of $(C_{13}H_9$-*cyclo*-C_6H_{10}-$O)LaI_2(DME)_2$

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Racemic *trans*-2-(9(H)-fluoren-9-yl)cyclohexanol, $C_{13}H_9$-*cyclo*-C_6H_{10}-OH (**1**), reacts with two equivalents of potassium naphthalenide in THF to give the dipotassium salt $[C_{13}H_8$-*cyclo*-C_6H_{10}-$O]K_2(THF)$ (**2**). Recrystallization of **2** from pyridine affords the solvent free salt $[C_{13}H_8$-*cyclo*-C_6H_{10}-$O]K_2$ (**3**). The reactions of $LaI_3(THF)_4$ with one equivalent of **2** or of $YbI_2(THF)_2$ with equimolar amounts of **2** produce the alkoxolanthanum diiodide $(C_{13}H_9$-*cyclo*-C_6H_{10}-$O)LaI_2(DME)_2$ (**4**) and the ytterbium dialkoxide $(C_{13}H_9$-*cyclo*-C_6H_{10}-$O)_2Yb(THF)_{0.5}$(**5**), respectively. $[(Me_3Si)_2N]_3Y$ reacts with three equivalents of **1** with elimination of hexamethyldisilazane and formation of the yttrium trialkoxide $(C_{13}H_9$-*cyclo*-C_6H_{10}-$O)_3Y$ (**6**). The compounds **2** to **5** were characterized by elemental analyses, ^1H NMR, ^{13}C NMR and IR spectra. The molecular structure of **4** was determined by single crystal X-ray diffraction.

Key words: Yttrium, Lanthanum, Ytterbium, Lanthanide(fluorenyl)alkoxides

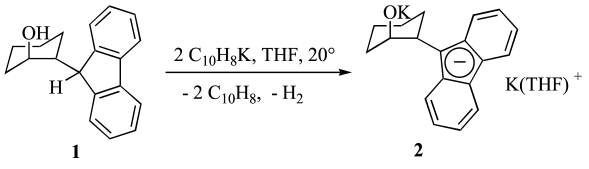
Introduction

During the last few years, half-sandwich complexes of the lanthanides met with great interest in organometallic chemistry, especially in polymerization catalysis, due to their electron deficiency and their steric accessibility [1]. The synthesis of such complexes containing η^5-cyclopentadienyl as well as anionic η^1-bonded ligands often is hampered by ligand redistribution reactions in solution. New ligand systems containing the η^5- and the η^1-functions in one and the same molecule can be expected to help to solve this problem. The successful use of *e. g.* the silyl-linked cyclopentadienyl-amido ligand $[(\eta^5$-$C_5Me_4)Me_2Si(\eta^1$-$NR)]^{2-}$, introduced by Bercaw *et al.* [2] into d- and f-transition metal chemistry, confirmed this supposition. Alkyl and hydrido complexes of group III metals with linked cyclopentadienyl-amido ligands show high activity as single-component catalysts for the polymerization of olefinic [2, 3a] and polar monomers [3b, 3c], for olefin hydrosilylation [4], and for the cyclization / hydroamination of α,ω-aminoolefins [5]. Further investigations clearly demonstrated that an extension of the molecular unit connecting the η^5- and the η^1-functional groups in such bidentate ligands has a dramatical influence on the structure and the reactivity of the corresponding complexes [4, 6, 7]. Besides the silyl-linked cyclopentadienyl-amido systems, linked cyclopentadienyl-alkoxo ligands were used to stabilize half-sandwich lanthanide complexes [8], although this class of compounds has been studied much less.

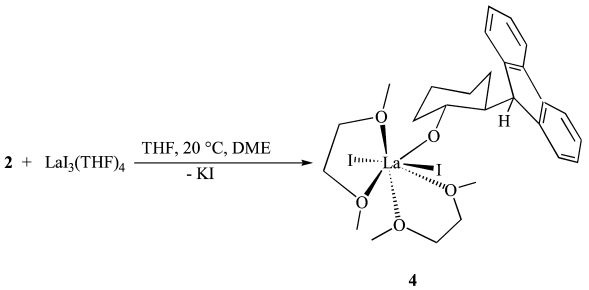
The aim of our present research was to investigate if the dianion of *trans*-2-(9(H)-fluoren-9-yl)cyclohexanol, $[2$-$(C_{13}H_8)$-*cyclo*-C_6H_{10}-$O]^{2-}$, can behave as a bidentate ligand towards lanthanide halides and if the free ligand 2-$C_{13}H_9$-*cyclo*-C_6H_{10}-OH will react with lanthanide silylamides with liberation of silylamine to form the corresponding lanthanide half-sandwich complexes in both cases.

Results and Discussion

trans-2-(9(H)-Fluoren-9-yl)-cyclohexanol, 2-$(C_{13}H_9)$-*cyclo*-C_6H_{10}-OH (**1**) was obtained as a racemic mixture by the reaction of epoxycyclohexane with



Scheme 1.



Scheme 2.

fluorenyllithium [9]. Compound **1** can be easily deprotonated by potassium naphthalenide in THF at room temperature to give the dipotassium salt [2-($C_{13}H_8$)-*cyclo*-C_6H_{10}-O]K_2(THF) (**2**) in yields of 85% (Scheme 1). Immediately after mixing the reagents, the deep green color of the solution caused by the $[C_{10}H_8]^{-\bullet}$ radical anion disappeared and fine, bright red crystals of **2** separated from the solution.

Compound **2** is hardly soluble in THF or DME. Recrystallization from pyridine afforded ruby-red crystals of the solvent free salt [$C_{13}H_8$-*cyclo*-C_6H_{10}-O]K_2 (**3**). The IR, ^{1}H and ^{13}C DEPT NMR spectra of **2** and **3** proved the deprotonation of both the hydroxyl group and the fluorenyl ring in position 9. The exact determination of the crystal and molecular structure of **3** by single crystal X-ray diffraction failed because of the poor quality of the crystals.

The treatment of $LaI_3(THF)_4$ with equimolar amounts of **2** in THF at 0 to 20 °C afforded a solid product which after its recrystallization from DME was characterized as the mixed-ligand alkoxolanthanum iodide complex [2-($C_{13}H_9$)-*cyclo*-C_6H_{10}-O]$LaI_2(DME)_2$ (**4**) (Scheme 2).

The colorless crystals of **4**, isolated in a yield of 39%, are soluble in THF and DME, but insoluble in aromatic and aliphatic hydrocarbons. The signals of the ^{1}H, ^{13}C DEPT, ^{1}H-^{1}H and ^{1}H-^{13}C NMR COSY spectra of **4** can be readily assigned. The ^{1}H NMR spectrum of **4** shows a set of two multiplets in the aromatic region due to the eight protons of the six-membered rings of the fluorenyl unit, a complex pattern of signals in the range 0.2 to 2.4 ppm, due to the methylene protons of the *cyclo*-hexyl moiety, and two multiplets at 2.15 and 4.16 ppm, caused by the two CH-$C_{13}H_9$ and CHO methine protons of the cyclohexyl group. The doublet at 4.98 ppm ($^3J_{H-H}$ = 2.3 Hz) proves the presence of a proton in position 9 of the fluorenyl fragment, thus indicating that this fragment is not coordinated to the lanthanum atom. The low value of the vicinal H-H coupling constant reflects a torsion angle H-C-C-H close to 90 °.

Table 1. Crystal data and structure refinement for **4**.

Empirical formula	$C_{27}H_{39}I_2LaO_5$
M_r [g mol^{-1}]	836.29
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
Unit cell dimensions	
a [Å]	8.5956(1)
b [Å]	26.5320(4)
c [Å]	13.8649(2)
β [°]	96.159(1)
V [Å^3]	3143.76(8)
Z	4
ρ_{calcd} [g/cm^3]	1.767
$[\mu]$ (Mo-K$_\alpha$) [mm^{-1}]	3.354
F(000)	1616
Crystal dimensions [mm^3]	0.39 × 0.28 × 0.16
θ(°) Range	1.54 → 27.50
Index ranges h	−11 → 10
k	−34 → 25
l	−18 → 18
Reflections collected	23469
Independent reflections	7166 [R(int) = 0.0772]
Reflections with $I > 2\sigma(I)$	5050
Max. / min. transmission	0.6775 / 0.4703
Goodness-of-fit on F^2	1.101
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0588, wR_2 = 0.0941
R indices (all data)	R_1 = 0.0973, wR_2 = 0.1046
Larg. diff. peak and hole [e/Å^3]	0.934 and −1.464

The solid state structure of **4** was determined by single crystal X-ray diffraction. Suitable crystals are obtained by slow concentration of DME solutions of **4** at room temperature. Compound **4** crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. The crystallographic data are summarized in Table 1 and the molecular structure is depicted in Fig. 1. The lanthanum atom is coordinated by two iodine atoms, the oxygen atom of the 2-(fluoren-9-yl)-*cyclo*-hexanolate ligand, and the four oxygen atoms of

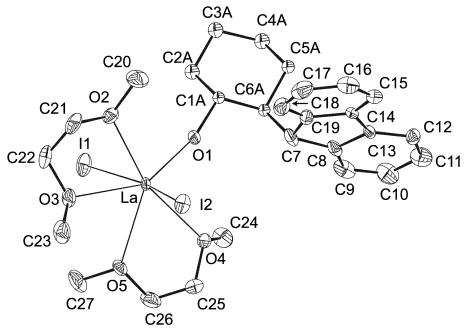


Fig 1. ORTEP drawing [10] and numbering scheme of the molecular structure of **4** (30% probability thermal ellipsoids); all hydrogen atoms and the disorder of the *cyclo*-hexyl ring have been omitted for clarity; selected bond lengths (Å) and angles (°): La-I(1) 3.2147(7), La-I(2) 3.1781(6), La-O(1) 2.124(5), La-O(2) 2.602(5), La-O(3) 2.665(5), La-O(4) 2.579(5), La-O(5) 2.649(5), I(1)-La-I(2) 164.944(19), I(1)-La-O(1) 92.76(14), I(1)-La-O(2) 89.77(12), I(1)-La-O(3) 83.41(12), I(1)-La-O(4), 105.94(12), I(1)-La-O(5) 82.96(14), I(2)-La-O(1) 98.93(14), I(2)-La-O(2) 81.90(12), I(2)-La-O(3) 81.64(12), I(2)-La-O(4) 85.18(12), I(2)-La-O(5) 93.69(14), O(1)-La-O(2) 84.92(19), O(1)-La-O(3) 147.8(2), O(1)-La-O(4) 82.01(18), O(1)-La-O(5) 140.99(19), O(2)-La-O(3) 63.19(18), O(2)-La-O(4) 159.95(17), O(2)-La-O(5) 133.58(17), O(3)-La-O(4) 129.82(18), O(3)-La-O(5) 70.43(18), O(4)-La-O(5) 62.38(16).

the two DME molecules. The coordination geometry around the lanthanum atom corresponds to a distorted pentagonal bipyramid with the two iodine atoms in axial positions and the five oxygen atoms occupying the equatorial plane.

The La-I (3.18/3.21 Å) and La-O(DME) (2.58 to 2.67 Å) distances in **4** are somewhat longer than those reported for $LaI_3(THF)_4$ (La-I: 3.13 to 3.19 Å; La-O(THF): 2.52 to 2.58 Å) [11]. As in **4**, the lanthanum center of $LaI_3(THF)_4$ is coordinated in a distorted pentagonal bipyramidal fashion with the two iodine atoms in the axial positions. In both compounds the angle between the axial iodine atoms and the central lanthanum atom deviates from the ideal value of 180° (**4**: 164.9°; $LaI_3(THF)_4$: 171.4°). Compared to the La-O distances of the coordinating DME oxygen atoms (average 2.62 Å), the distance between the lanthanum atom and the covalently bonded *cyclo*-hexanolate oxygen atom is much shorter (2.12 Å). Slightly longer La-O distances for covalently bonded oxygen atoms were observed in *e. g.* $(Ph_3SiO)_3La(THF)_3$ (2.20 to 2.25 Å) [12], (2,6-$Ph_2C_6H_3O)_3La(THF)_2$ (2.23 to 2.25 Å) [13], and $[(Ph_3CO)_2La(\mu\text{-}OCPh_3)]_2$ (La-O 2.18 Å; La-(μ-O) 2.39/2.48 Å) [14]. The carbon atoms of the *cyclo*-hexyl ring in **4** are disordered about two positions (A and B) with occupancy factors of 0.721(12) (A) and 0.279(12) (B). Bond distances and angles of the two parts were restrained to be equal. The six-membered ring adopts a chair conformation.

The formation of **4** can be rationalized by the initial formation of the actually expected complex [2-(η^5-$C_{13}H_8$)-*cyclo*-C_6H_{10}-η^1-O]LaI(THF)$_n$ with the fluorenylalkoxo groups acting as a bidentate ligand followed by transformation of this sterically constrained intermediate into **4** by detaching the η^5-$C_{13}H_8$-La coordination with simultaneous reception of a proton by the $C_{13}H_8$ moiety, probably abstracted from THF.

Recently we reported on the synthesis and crystal structure of the related cyclopentadienyl-alkoxo complexes $\{[(\eta^5\text{-}C_5H_4)CH_2CH(\mu^3\text{:}\eta^1\text{-}O)CH_2OBu]Yb\}_4$ [8d] and $\{[(\eta^5\text{-}C_5H_4)CH_2CH(\mu^2\text{:}\eta^1\text{-}O)CH_2OBu]LaN(SiMe_3)_2\}_2$ [8e] in which the η^5-Cp- and the η^1-O functions of the ligand are separated by the same number of carbon atoms as in the [2-($C_{13}H_8$)-*cyclo*-C_6H_{10}-O]$^{2-}$ dianion. Both complexes are stable in the solid state as well as in solution up to temperatures of 60 °C. Obviously, steric reasons and the lack of a third *Lewis*-basic donor group as it is present in the ligand system of the above mentioned complexes, prevent the [2-($C_{13}H_8$)-*cyclo*-C_6H_{10}-O]$^{2-}$ dianion from acting as a bidentate ligand.

Protonation of the $C_{13}H_8$ ring system was also observed in the reaction of equimolar amounts of $YbI_2(THF)_2$ and **2** in THF at 0 to 20 °C (Scheme 3). Along with approximately half of the amount of $YbI_2(THF)_2$ used in the reaction, a yellowish brown powder was isolated, the spectroscopic data of which correspond to the formula [2-($C_{13}H_9$)-*cyclo*-C_6H_{10}-O]$_2$Yb(THF)$_n$ ($n \leq 2$). Removal of the incorporated solvent in vacuum at 20 °C for 2 h afforded [2-($C_{13}H_9$)-*cyclo*-C_6H_{10}-O]$_2$Yb(THF)$_{0.5}$ (**5**) as indicated by IR, ^{1}H and ^{13}C NMR measurements.

$$2\ \mathbf{2} + YbI_2(THF)_2 \xrightarrow[-2\ KI]{THF,\,20\ ^\circ C} [2\text{-}C_{13}H_9\text{-}c\text{-}C_6H_{10}O]_2Yb(THF)_{0.5}\ (\mathbf{5})$$

Scheme 3.

As already observed for the lanthanum derivative **4**, the [2-($C_{13}H_8$)-*cyclo*-C_6H_{10}-O]$^{2-}$ dianion does not behave as a bidentate ligand. It can be supposed that protonation of the $C_{13}H_8$-unit and formation of [2-($C_{13}H_9$)-*cyclo*-C_6H_{10}-O]YbI(THF)$_n$ are the first steps in this reaction. The formation of **5** as well as the recovery of half of the amount of $YbI_2(THF)_2$ used in

the reaction are the result of the disproportionation of the alkoxo-iodide. Mixed ligand complexes of divalent ytterbium are known to be predisposed to disproportionate in solution.

The elimination of hexamethyldisilazane from homoleptic $[(Me_3Si)_2N]_nLn$ (Ln/*n* = Sm/2, Yb/2, Nd/3, Sm/3, Lu/3) by treatment with $Me_2Si(C_5Me_4H)(NHR)$ (R = ^{t}Bu [15a], Ph [15b]) or $RHCH_2CH(OH)CH_2OBu$ (R = C_5H_4, 3-C_9H_6) [8e] turned out to be a convenient method for the synthesis of lanthanide amido or alkoxo half-sandwich complexes. We tried to use this method in order to synthesize [2-(η^5-$C_{13}H_8$)-*cyclo*-C_6H_{10}-η^1-O]YN(SiMe$_3$)$_2$ by reacting equimolar amounts of **1** and $[(Me_3Si)_2N]_3Y$ in toluene at 60 °C. Under the cited conditions the reaction affords a non separable mixture of products which, according to ^{1}H NMR spectroscopic data, contains the fluorenyl ligand still in the protonated and thus non-coordinating fashion. When the reaction of $[(Me_3Si)_2N]_3Y$ with **1** is carried out in a molar ratio of 1:3 in toluene at 80 °C, three equivalents of $(Me_3Si)_2NH$ are liberated. Recrystallization of the crude off-white solid isolated from the reaction mixture from hot hexane affords [2-($C_{13}H_9$)-*cyclo*-C_6H_{10}-O]$_3$Y (**6**) as a colorless crystalline powder in a yield of 83% (Scheme 4). Compound **6** is soluble in ethers, aromatic hydrocarbons, and hot hexane. The ^{1}H NMR spectrum of **6** recorded at 20 °C shows noticeably broadened signals. The reason for this broadening is the restricted rotation of the three ligands as a consequence of their bulkiness.

$$[(Me_3Si)_2N]_3Y + 3\ \mathbf{1} \xrightarrow[-3\ (Me_3Si)_2NH]{\text{toluene, 60 °C}} [2\text{-}C_{13}H_9\text{-}c\text{-}C_6H_{10}\text{-}O]_3Y\ (\mathbf{6})$$

Scheme 4.

At this point it should be noted that the reaction of $[(Me_3Si)_2N]_3Y$ with 3 equivalents of 2-(fluoren-9-yl)ethanol also leads to elimination of three equivalents of $(Me_3Si)_2NH$, but the product formed is insoluble in organic solvents.

The results reported above clearly demonstrate that in contrast to the cyclopentadienyl-alkoxo and -siloxo ligands $[C_5H_4CH_2CH(O)CH_2OBu]^{2-}$ [8d,8e], $[C_5H_4CH_2CH(O)R]^{2-}$ [8a,8c], and $[C_5Me_4SiMe_2OSiMe_2O]^{2-}$ [8b], the [2-($C_{13}H_8$)-*cyclo*-C_6H_{10}-O]$^{2-}$ dianion does not act as a bidentate ligand towards Y(III), La(III), and Yb(II) ions. This fact is due to the more bulky fluorenyl and *cyclo*-hexyl moieties and to the rigidity of the system caused by its *trans*-configuration.

Experimental Section

All experiments were carried out under rigorous exclusion of moisture and air in evacuated tubes using standard Schlenk techniques. THF, DME, toluene, and hexane were purified by distillation from sodium/benzophenone ketyl and were condensed in vacuum prior to use. $LaI_3(DME)_4$ [16], $YbI_2(THF)_2$ [17], and $[(Me_3Si)_2N]_3Y$ [18] were prepared according to literature procedures. The IR spectra were recorded as Nujol mulls on a Specord M80 spectrophotometer. The NMR spectra were recorded on a Bruker DPX200 spectrometer. The chemical shift values were referenced internally to residual solvent resonances and reported in ppm relative to TMS. GC analyses were performed using the Tzvet 530 gas chromatograph.

*[$C_{13}H_8$-cyclo-C_6H_{10}-O]K_2(THF) (**2**):* A solution of **1** (0,31 g, 1,17 mmol) in THF (5 ml) was slowly added at room temperature to a solution of K[$C_{10}H_8$] obtained by reacting $C_{10}H_8$ (0,30 g, 2,34 mmol) with K (0,092 g, 2,34 mmol) in THF (10 ml). The color of the reaction mixture turned from deep-green to bright-red and red crystals grew up slowly. After standing of the reaction mixture overnight, the liquid part was decanted. The remaining crystals were washed twice with cold THF and dried *in vacuo* at room temperature for 2 h to afford **2** (0,41 g (85,4%) as red crystals. – IR (Nujol, KBr): 3050 (m), 1580 (m), 1320 (s), 1210 (m), 1050 (s), 860 (m), 790 (s), 760 (s), 720 cm^{-1} (s). – ^{1}H NMR (200 MHz, [D$_5$]pyridine, 293 K): δ = 0.77 – 1.76 [m, 10 H, C*H*$_2$(C_6H_{10}), β-C*H*$_2$(THF)], 1.80 (m, 2 H, C*H*$_2$CHO), 2.11 (m, 1 H, C*H*-Flu), 3.64 [m, 4 H, α-C*H*$_2$(THF)], 4.20 (m, 1 H, C*H*O), 6.99 – 8.71 (m, 8 H, Flu). – ^{13}C{^{1}H} NMR (50 MHz, [D$_5$]pyridine, 293 K): δ = 25.6 [β-*C*H$_2$(THF)], 26.6, 27.8, 33.7 [all C*H*$_2$(C_6H_{10})], 39.5 (*C*H$_2$CHO), 47.3 [*C*-9(Flu)], 50.1 (*C*H-Flu), 67.6 [α-*C*H$_2$(THF)], 71.6 (*C*HO), 98.8, 108.9, 109.2, 112.0, 116.7, 119.6, 120.1, 120.9 [all *C*-1,2,3,4,5,6,7,8(Flu)], 131.5, 133.3, 136.1, 139.3 [all *C*-10,11,12,13(Flu)]. – $C_{23}H_{26}K_2O_2$ (412.65): calcd. C 66.95, H 6.35, K 18.95; found C 66.63, H 6.71, K 18.73.

*[$C_{13}H_8$-cyclo-C_6H_{10}-O]K_2 (**3**):* The solution of **2** (0,24 g, 0,58 mmol) in pyridine (10 ml) was heated to 60 °C for 2 h. The hot solution was concentrated *in vacuo* to half of its volume. Then pyridine (10 ml) was added again, and the solution heated to 60 °C for further 6 h. Subsequent slow cooling of the mixture to ambient temperature caused the separation of **3** (0,19 g, 95%) as ruby red crystals. – IR (Nujol, KBr): 3050 (m), 1580 (m), 1320 (s), 1210 (m), 1030 (s), 790 (s), 760 (s), 720 cm^{-1} (s). – ^{1}H NMR (200 MHz, [D$_5$]pyridine, 293 K): δ = 0.64 – 1.70 [m, 6 H, C*H*$_2$(C_6H_{10})], 1.73 (m, 2 H, C*H*$_2$CHO), 2.17 (m, 1 H, C*H*-Flu), 4.29 [m, 1 H, C*H*O), 6.92 – 8.66 (m, 8 H, Flu). – ^{13}C{^{1}H} NMR (50 MHz, [D$_5$]pyridine, 293 K): δ = 27.0, 27.6, 33.5 [all C*H*$_2$(C_6H_{10})], 39.2 (*C*H$_2$CHO), 47.3 [*C*-9(Flu)], 50.7 (*C*H-Flu), 71.1 (*C*HO), 98.1, 108.0, 109.2, 113.4, 117.4, 120.0, 120.9, 122.4 [all *C*-1,2,3,4,5,6,7,8(Flu)], 132.9, 133.7, 138.2,

139.3 [all *C*-10,11,12,13(Flu)]. – $C_{19}H_{18}K_2O$ (340.55): calcd. C 67.01, H 5.33, K 22.96; found C 66.67, H 5.81, K 23.16.

($C_{13}H_9$-cyclo-C_6H_{10}-O)LaI$_2$(DME)$_2$ ***(4):*** Compound **2** (0,54 g, 1,32 mmol) was slowly added to a suspension of $LaI_3(THF)_4$ (1,07 g, 1,32 mmol) in THF (40 ml) at 0 °C with vigorous stirring. The reaction mixture was allowed to warm up to room temperature and to stand for 12 h. The precipitated KI was filtered off, the solvent was removed *in vacuo*, and the remaining off-white residue was dissolved in DME. Slow evaporation of the solution at room temperature gave colorless crystals of **4** (0,43 g, 39%). M. p. 186 °C dec. – IR (Nujol, KBr): 3050 (m), 1590 (m), 1340 (s), 1210 (m), 1060 (s), 790 (s), 760 (s), 720 cm^{-1} (s). – ^{1}H NMR (200 MHz, [D$_8$]THF, 293 K): δ = 0.30 – 1.64 [m, 6 H, C*H*$_2$(C_6H_{10})], 1.84 (m, 2 H, C*H*$_2$CHO), 2.15 (m, 1 H, C*H*-Flu), 3.26 [s, 12 H, C*H*$_3$(DME)], 3.49 [s, 8 H, C*H*$_2$(DME)], 4.16 (m, 1 H, C*H*O), 4.98 [d, ^3J = 2.3 Hz, 1 H, 9-*H*(Flu)], 7.15 – 7.34 (m, 4 H, Flu), 7.59 – 7.78 (m, 4 H, Flu). – ^{13}C{^{1}H} NMR (50 MHz, [D$_8$]THF, 293 K): δ = 24.8, 26.4, 26.7 [all C*H*$_2$(C_6H_{10})], 40.8 (*C*H$_2$CHO), 48.3 [*C*-9(Flu)], 52.8 (*C*H-Flu), 58.8 [*C*H$_3$(DME)], 72.6 [*C*H$_2$(DME)], 79.6 (*C*HO), 119.8, 120.3, 124.8, 126.7, 127.0, 127.1, 127.4, [all *C*-1,2,3,4,5,6,7,8(Flu)], 142.5, 142.9, 146.7, 149.3 [all *C*-10,11,12,13(Flu)]. – $C_{27}H_{39}I_2LaO_5$ (836.32): calcd. I 30.35, La 16.61; found I 30.75, La 16.83.

($C_{13}H_9$-cyclo-C_6H_{10} – O)$_2$Yb(THF)$_{0.5}$ ***(5):*** Compound **2** (0,44 g, 1,06 mmol) was slowly added to a suspension of $YbI_2(THF)_2$ (0,61 g, 1,06 mmol) in THF (25 ml) at 0 °C under vigorous stirring. The reaction mixture was allowed to warm to room temperature and stirred for 12 h. The precipitated KI was filtered off, then the solution was concentrated to the third of its initial volume. Cooling of this solution to 0 °C caused the separation of a greenish-yellow crystalline solid which was isolated by decantation. The solid was washed with cold THF and dried *in vacuo* at 50 °C to give $YbI_2(THF)_2$ (0,27 g, 44%). – IR (Nujol, KBr): 1050 (m), 860 cm^{-1} (m). – The decanted THF solution was evaporated *in vacuo* leaving a brown solid which was extracted three times with a hot toluene-hexane mixture (v/v 1:1, 3 × 15 ml). Cooling of the combined extracts to 0 °C produced a yellowish-brown amorphous powder. The powder was washed with cold hexane and dried *in vacuo* for 2 h to give **5** (0,20 g, 51% with respect to **2**). M. p. 136 °C dec. – IR (Nujol, KBr): 3050 (m), 1570 (m), 1310 (s), 1130 (m), 1090 (s), 1050 (m), 850 (m), 780 (s), 740 (s), 720 cm^{-1} (s). – ^{1}H NMR (200 MHz, [D$_5$]pyridine, 293 K): δ = 0.73 [m, 2 H, C*H*$_2$(C_6H_{10})], 1.13 [m, 2 H, C*H*$_2$(C_6H_{10})], 1.51 [m, 2 H, C*H*$_2$(C_6H_{10})], 1.70 (s$_{br}$, 2 H, THF), 2.15 (m, 2 H, C*H*$_2$CHO), 3.04 (m, 1 H, C*H*-Flu), 3.61 (m, 1 H, C*H*O), 3.67 (s$_{br}$, 2 H, THF), 4.55 [s$_{br}$, 1 H, 9-H(Flu)], 6.84 – 7.74 (m, 4 H, Flu), 8.25 – 8.51 (m, 4 H, Flu). – ^{13}C{^{1}H} NMR (50 MHz, [D$_5$]pyridine, 293 K): δ = 22.7, 23.4, 25.9 [all *C*H$_2$(C_6H_{10})], 26.8 (THF), 39.7 (*C*H$_2$CHO), 47.6 [*C*-9(Flu)], 52.0 (*C*H-Flu), 68.9 (THF), 78.1 (*C*HO), 118.7, 119.9, 123.9, 125.7, 126.0, 127.1, [all *C*H(Flu)], 141.5, 141.9, 145.7, 148.3 [all *C*- 10,11,12,13(Flu)]. – $C_{40}H_{42}O_{2.5}Yb$ (735.81): calcd. C 65.29, H 5.75, Yb 23.52; found C 64.73, H 5.99, Yb 23.60.

($C_{13}H_9$-cyclo-C_6H_{10}-O)$_3$Y ***(6):*** Compound **1** (1,63 g, 6,16 mmol) was added to a solution of $[(Me_3Si)_2N]_3Y$ (1,17 g, 2,05 mmol) in toluene (40 ml) at room temperature. The reaction mixture was heated to 80 °C for 12 h and the volatiles condensed in a cooled trap. After that, a new portion of toluene (40 ml) was added and the solution was heated for further 6 h simultaneously condensing the volatiles. The last procedure was repeated once again leaving an off-white solid. The combined condensates contained hexamethyldisilazane (0,90 g, 91%) as estimated by GC. The off-white solid was recrystallized from hexane to give **6** (1,50 g, 83%) as a white microcrystalline powder. M. p. 177 °C dec. – IR (Nujol, KBr): 3050 (m), 1600 (m), 1320 (m), 1300 (m), 1150 (s), 1110 (s), 1040 (s), 750 (s), 720 (s), 700 cm^{-1} (s). – ^{1}H NMR (200 MHz, [D$_6$]benzene, 293 K): δ = 0.58 – 1.71 [m, 6 H, C*H*$_2$(C_6H_{10})], 2.31 [m, 2 H, C*H*$_2$CHO), 2.52 (m, 1 H, C*H*-Flu), 4.49 (s$_{br}$, 1 H, C*H*O), 5.22 [s$_{br}$, 1 H, 9-H(Flu)], 7.25 – 7.50 (m, 4 H, Flu), 7.68 – 7.91 (m, 4 H, Flu). – ^{13}C{^{1}H} NMR (50 MHz, [D$_6$]benzene, 293 K): δ = 24.7, 26.2, 30.9 [all *C*H$_2$(C_6H_{10})], 39.2 (*C*H$_2$CHO), 47.3 [*C*-9(Flu)], 51.7 (*C*H-Flu), 76.1 (*C*HO), 118.9, 119.4, 125.2, 125.9 [all *C*H(Flu)], 141.0, 141.5, 144.7, 147.0 [all *C*-10,11,12,13(Flu)]. – $C_{57}H_{57}O_3Y$ (878.98): calcd. C 77.89, H 6.54, Y 10.11; found C 78.29, H 6.69, Y 9.90.

Crystal structure determination: Crystals suitable for single crystal X-ray diffraction were obtained from DME. The crystal and structure refinement data are listed in Table 1. The data were collected on a Siemens SMART CCD diffractometer with area detector (graphite monochromator, Mo-K$_\alpha$ radiation, λ = 0.71073 Å) by use of ω scans at 173 K. The structure was solved by direct methods and was refined on F^2 with the SHELX-97 software package [19] using all reflections. All non hydrogen atoms were refined anisotropically. The carbon atoms of the disordered part were refined isotropically. The hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å^2. The idealized methyl groups were allowed to rotate about their X-C bond. SADABS [20] was used to perform area-detector scaling and absorption corrections. The maximum and minimum transmission factors are given in Table 1. The PLATON program [21] was used for the geometric analysis of the structure. The crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-196127. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: +44 (0)1223-336-033; email: deposit@ccdc.cam.ac.uk.

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